A Comparison of Chemical and Electrolytic Methods of Reduction.

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It is shown that there is a close relation between reduction by dissolving metals and electrolytic reduction, and that in favourable instances the rate of the former process can be predicted from electrolytic reduction data. This was confirmed experimentally for the reduction of a number of substances by zinc amalgam, zinc, and cadmium.

By determining the yields of the various products obtained on the reduction of diene acids, Isaacs and Wilson (*J.*, 1936, 202, 574, 810; *Trans. Electrochem. Soc.*, 1939, **75**, 353) were able to distinguish two types of electro-reduction: (*A*) those at smooth cathodes, where reduction is similar to that by dissolving metals, and (*B*) those at cathodes of spongy nickel and of platinised platinum, where reduction is similar to catalytic hydrogenation. These conclusions are supported by the many isolated examples of such similarities that have been reported. The aim of this work is to provide a closer correlation of the two types of reducing systems in (*A*).

On the basis of the electrochemical theory of the corrosion of metals in conducting solutions the reaction

$$M + zH^+ \longrightarrow M^{z+} + \tfrac{z}{2}H_2$$

occurs as the result of two processes. At the anodic areas of the metal surface, the metal dissolves

$$M - ze \longrightarrow M^{z+}$$

and at the cathodic areas hydrogen ions are reduced

$$zH^+ + ze \longrightarrow \tfrac{z}{2}H_2$$

The hydrogen is formed by electrochemical action and the electrode potential of the cathodic areas is governed by the same factors as those which apply to the discharge of hydrogen at a normal cathode of the same material.

If a reducible substance (Ox) is added, the reaction is changed; some or all of the hydrogen ions previously liberated as molecular hydrogen react with the depolariser, *e.g.*:

$$Ox + nH^+ + ne \longrightarrow OxH_n$$

or $Ox + nH^+ + ne \longrightarrow Red + \tfrac{n}{2}H_2O$ where Red signifies the reduced form.*

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* The treatment given also applies to reduction reactions that can be formulated without hydrogen ions, *e.g.*, $Fe^{3+} + e \longrightarrow Fe^{2+}$.

The metal dissolves more rapidly than in the absence of the depolariser, but by the same process. The reduction of the depolariser takes place at cathodic areas, which may be different from those previously operating, while the reaction at the anodic areas remains the same.

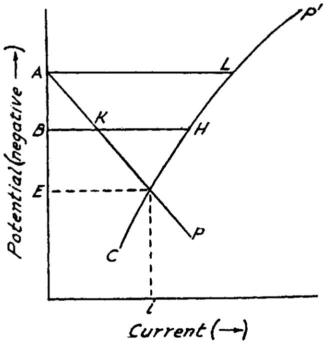
On this basis, the reduction of a substance by dissolving metals in conducting solutions proceeds by electrochemical means, but no assumptions are made concerning the mechanism of electrolytic reduction. In the sections below, it is shown how the rate of chemical reduction may be predicted from purely electrolytic data, and the experimental work serves to test the conclusions reached. Two sets of conditions will be considered.

(I) *The Dissolving Metal has a Uniform Surface.*—The material studied, namely, liquid zinc amalgam, will be chosen as a specific example. Wagner and Traud (*Z. Elektrochem.*, 1938, **44**, 391) studied the reaction of zinc amalgam with acids and concluded that, although spatially separated anodic and cathodic areas do not exist on this material, an electrochemical mechanism of dissolution is still operative; almost the whole of the surface of the amalgam is acting as a cathode, and the anodic reaction is not restricted to any particular part of the surface, but occurs first at one point and then at another.

By obtaining values for the rate of reduction (I') and the cathode potential (e) for the electro-reduction of a given substance at zinc amalgam, it is possible, by an extrapolation of the e–log I' curve, to find the value of I' at the potential of the zinc amalgam when it is dissolving freely in the presence of the reducible substance. According to the argument presented above, this rate should be equal to the rate of chemical reduction.

In this instance, a simplification is possible. The overpotential behaviour of dilute liquid zinc amalgam is almost identical with that of pure mercury. Hence, the predicted rate of chemical reduction can be obtained from the appropriate e–log I' curve for mercury by interpolation.

This simplified procedure was used by Wagner and Traud for the reduction of hydrogen ions to molecular hydrogen, and good agreement between the predicted and the observed rates of chemical reduction was obtained. In the experimental section, this work is extended to the reduction of substances other than hydrogen ions, namely, maleic acid and potassium bromate.



(II) *The Dissolving Metal is Pure but its Surface is not Uniform.*—Dissolution of a pure solid metal may proceed to some extent by the mechanism indicated by Wagner and Traud but, because of the non-uniformity of the surface, spatially separated anodic and cathodic areas will also be operative. The cathodic areas will consist of portions of the metal that have a standard electrode potential and hydrogen overpotential *slightly* different from those of the metal in the anodic areas owing to differences in strain, crystal size, nature of crystal face exposed, etc.

The potential–current relations for such a system are represented graphically in the diagram (cf. Evans, " Metallic Corrosion, Passivity and Protection," Edward Arnold and Co., London, 1946, p. 256). It is assumed that metal ions are present in the solution when the potential of the metal is less negative than A, *i.e.*, when some " chemical " reduction is occurring, and that there are no metal ions present when the potential of the metal is more negative than A, *i.e.*, when the reduction is purely electrolytic. These conditions are those obtaining in the experimental work.

A–P represents the anodic polarisation curve; it may not be linear but for solutions that contain moderate quantities of simple metal ions the anodic polarisation is generally small. C–P' represents the cathodic polarisation curve.

When the metal is dissolving freely at a steady rate, the potentials of the anodic and the cathodic areas are equal [*] and given by E, and the current flowing (= rate of metal dissolution) is given by i.

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[*] Strictly, these potentials differ by iR, where i is the current passing between the two types of area and R is the resistance offered by the solution; for good-conducting solutions, such as were used in the experimental work, iR is negligible.

If the metal is now cathodically polarised so that conditions represented by B–K–H are reached, the rate of metal dissolution has decreased to B–K. The cathodic current flowing is B–H, made up of H–K, the externally applied current and B–K, the internal current. When conditions represented by A–L are reached, metal dissolution ceases and the cathodic current A–L is equal to the externally applied current, *i.e.*, the cathodic reaction is purely electrolytic. It may be considered that, up to this stage, the cathodic reaction has taken place on the original cathodic areas only. If, however, the potential of the metal is made more negative than A, cathodic reaction will also occur on areas hitherto anodic, because these are of the same material as the cathodic areas and have hydrogen overpotentials that are only slightly different. This change-over may take place progressively as the potential is made more negative than E, but should be complete at potentials more negative than A. In these circumstances, the current distribution on the various parts of the electrode surface will not be quite regular, but the effect can be neglected.

By extrapolation of electrolytic reduction results, the value of I' at the potential E can be obtained. This rate should be greater than the observed rate of chemical reduction by a factor equal to

$$\frac{\text{effective area of the whole cathode}}{\text{effective area of the cathodic portions of the dissolving metal}}$$

Unfortunately, there are no methods of obtaining this ratio, but it will be near unity for metals where the anodic polarisation is small, *e.g.*, zinc and cadmium in simple salt solutions.

This treatment has been tested experimentally for the reduction of maleic acid, sodium hydrogen sulphite, and titanic sulphate, at electrodes of spectrographically pure zinc and cadmium.

EXPERIMENTAL

Apparatus.—The reduction cell was constructed so that the anolyte and catholyte were prevented from mixing, and atmospheric oxygen was excluded. It consisted of an H-shaped vessel of Pyrex glass. The two vertical compartments, which held the anode and the cathode, were connected at their lower ends by a water-sealed tap that was kept closed during electrolysis. The cathode compartment, which had a volume of ~150 ml., was fitted with a water-sealed ground-glass cap, into which were sealed two narrow vertical tubes. These were ground to receive two sliding tubes that carried the electrode and a Luggin capillary; thus the electrode could be lowered into or raised from the solution and the capillary tip could be moved over the surface of the electrode without disturbing the rest of the apparatus. (Suitable modifications were made for experiments with liquid cathodes.) A burette was also sealed through the cap of the cathode compartment and a separate inlet tube for further reagents was provided so that, when necessary, titration of the solution after reduction could be carried out without opening the cell to the atmosphere. Stirring was effected by a stream of hydrogen, which entered at the bottom of the compartment and emerged through a " bubbler " above the level of the solution. The anode compartment was fitted with a ground-glass cap that carried the platinum anode. Gaseous anodic products were swept out of the anolyte by a stream of hydrogen.

The cell was immersed in a water-bath maintained at 25° ± 0·1°.

Electrodes.—The zinc and cadmium were " spectrographically standardised " rods supplied by Johnson, Matthey and Co., Ltd. Before use, the electrodes were rubbed with fine glass-paper, washed with conductivity water, etched in 5N-hydrochloric acid for 5 min., washed again with conductivity water, and finally kept in a sample of the solution to be studied until required. Mercury was distilled twice and finally purified by Brummer and Náray-Szabó's method (*Z. Elektrochem.*, 1925, **31**, 95).

Reagents, Analysis, etc.—All solutions were prepared with conductivity water. 0·1N-Solutions of the reducible compounds were prepared in one of three supporting electrolytes; (I) N-acetic acid–N-sodium acetate; (II) N-sulphuric acid; (III) N-potassium chloride.

Maleic acid solutions were prepared from maleic anhydride that had been crystallised from chloroform. Maleic acid was determined by Lucas and Pressman's method (*Ind. Eng. Chem. Anal.*, 1938, **10**, 140). Potassium bromate was determined iodometrically. The sodium hydrosulphite (dithionite) formed by the reduction of sodium hydrogen sulphite was determined by

Merriman's method (*J. Soc. Chem. Ind.*, 1923, **42**, 290). Titanic sulphate solutions were prepared by the decomposition of recrystallised potassium titanyl oxalate with sulphuric acid, followed by suitable dilution. The tervalent titanium formed on reduction was determined by adding ferric alum and titrating the resultant ferrous iron with 0·1N-potassium permanganate.

The presence of the reduction products had no effect on the rate of reduction at a given potential. In some of the chemical reductions, sufficient of the appropriate metal salt was added to give an approximately 0·1M-solution. The potential of the dissolving metal was, however, stable without this addition.

Hydrogen used for stirring was passed over palladised asbestos at 350° to remove the bulk of the oxygen; after being cooled, it was passed through a sample of the solution in use and thence to the cell.

Electrical Measurements.—Current densities of between 10^{-4} and 5×10^{-2} amp./sq. cm. and electrode areas of between 20 and 1 sq. cm. were employed. The Luggin capillary was connected either to a hydrogen electrode dipping into a sample of the supporting electrolyte or to a normal calomel electrode. The e.m.f. of the cell cathode–reference electrode was measured to the nearest mv. Thus the cathode potential was determined as in the direct method for the determination of hydrogen overpotential.

General Procedure.—100 Ml. of the solution were placed in the cathode chamber, and ~50 ml. of the same solution in the anode chamber. The prepared cathode was placed in position above the solution, and assembly of the cell completed. After hydrogen had been passed through both compartments for 1 hr., the polarising source was switched on and the cathode lowered into the electrolyte. The current was immediately adjusted and electrolysis was allowed to proceed until approx. 10% of the depolariser had been reduced. During the electrolysis, the cathode potential was determined at frequent intervals. At the end of the electrolysis the cathode was raised from the electrolyte, and the polarising source switched off. Analysis of the reduced solution was then carried out on a suitable aliquot portion or, when necessary, *in situ*. Chemical reductions were carried out by similar means but without polarisation of the electrode or use of the anode chamber.

RESULTS

The cathode potential (e) rapidly attained a maximum negative value and then remained constant to within ±0·01 v over a period of hours. The mean value of e was taken in each case. The relation between e and the rate of reduction (I') of a given substance was of the form $-e = a + b' \log I'$ where a and b' are constants. The value of b' was in most cases about 0·1.

The predicted rates of chemical reduction, by zinc amalgam, of maleic acid and of potassium bromate were obtained by interpolation from the appropriate e–log I' lines for a mercury cathode. The predicted rates of chemical reduction for the other systems were obtained by extrapolation of the e–log I' lines for zinc and cadmium cathodes.

In the Tables below, the supporting electrolyte is indicated by the appropriate Roman numeral; i is the total current in milliamp.; A is the area of the cathode in sq. cm.; I is the cathodic current density in amp./sq. cm.; t is the time of electrolysis in hours; B is the amount of reduction in milliequivs.; and I' is the rate of reduction expressed as amp./sq. cm. The cathode potential, e, is expressed in mv relative to the reversible hydrogen-electrode potential in the supporting electrolyte used, except for the reductions of sodium hydrogen sulphite, where the cathode potential is on the hydrogen scale.

The values given represent the mean of duplicates in most cases; in duplicate experiments the cathode potentials observed for a given rate of reduction did not differ by more than 0·015 v. The difference between the logarithms of the predicted and the observed rates of reduction does not exceed 0·1, and this is therefore within the limits of experimental error.

DISCUSSION

The results, although limited in number, cover a range of rates of reduction and offer a verification of the treatment given. Reduction by dissolving metals in conducting solutions proceeds by electrochemical means but no assumptions have been made concerning the mechanism of electrolytic reduction.

Reduction by dissolving metals is usually, but not universally, regarded as taking place by successive addition of hydrogen ions and electrons to the reducible substance, whereas electro-reduction is frequently ascribed to the direct action of hydrogen atoms. The mechanism of both processes is, however, the same. If an " atomic hydrogen " theory of hydrogen overpotential is accepted, electroreduction must occur by reaction of the depolariser with atomic hydrogen. If a " slow discharge " theory of hydrogen overpotential is accepted, a mechanism of electroreduction based on the successive addition of

i	A	10^4I	$-e$	t	B	I'
(a) *Zinc amalgam electrodes.*						
		Reduction of maleic acid (I)				
30·4	1	304	607	—	—	*
9·7	1	97	510	—	—	*
3·05	1	30·5	467	—	—	*
0·97	1	9·7	437	—	—	*
0	1	0	550	1	0·56	$1·5 \times 10^{-2}$
						Predicted $1·8 \times 10^{-2}$
		Reduction of potassium bromate (I)				
1·36	1	13·6	747	3	0·15	$1·34 \times 10^{-3}$
3·03	1	30·3	785	—	—	*
0·98	1	9·8	734	—	—	*
0·097	1	0·97	625	—	—	*
0·0302	1	0·302	561	—	—	*
0·0096	1	0·096	508	—	—	*
0	12·56	0	556	38	0·50	$2·8 \times 10^{-5}$
						Predicted $2·6 \times 10^{-5}$
(b) *Zinc electrodes.*						
		Reduction of sodium hydrogen sulphite (III)				
40	4	100	1013	1·5	0·90	$4·03 \times 10^{-3}$
12	4	30	906	2	0·87	$2·91 \times 10^{-3}$
4	4	10	849	2	0·75	$2·51 \times 10^{-3}$
0	4	0	831	2	0·69	$2·3 \times 10^{-3}$
						Predicted $2·4 \times 10^{-3}$
		Reduction of maleic acid (I)				
4·7	1·14	42	580	1	0·94	$2·21 \times 10^{-2}$
0·46	1·14	4·2	558	1	0·78	$1·83 \times 10^{-2}$
0	1·14	0	545	1	0·77	$1·8 \times 10^{-2}$
						Predicted $1·6 \times 10^{-2}$
		Reduction of titanic sulphate (II)				
34	3·38	100	789	1	0·83	$6·58 \times 10^{-3}$
3·4	3·38	10	776	1	0·63	$5·0 \times 10^{-3}$
0·28	2·77	1	766	2	0·91	$4·4 \times 10^{-3}$
0	1·64	0	761	1·5	0·39	$4·3 \times 10^{-3}$
						Predicted $3·9 \times 10^{-3}$
(c) *Cadmium electrodes.*						
		Reduction of sodium hydrogen sulphite (III)				
12	4	30	770	1·5	0·61	$2·73 \times 10^{-3}$
4	4	10	630	2	0·38	$1·27 \times 10^{-3}$
0·4	4	1	549	2	0·31	$1·04 \times 10^{-3}$
0	4	0	539	2	0·36	$1·2 \times 10^{-3}$
						Predicted $1·0 \times 10^{-3}$
		Reduction of maleic acid (I)				
4·5	5	9	452	4	0·65	$8·72 \times 10^{-4}$
1·25	5	2·5	377	5	0·25	$2·68 \times 10^{-4}$
0·35	11·5	0·3	327	23	1·25	$1·27 \times 10^{-4}$
0	11·5	0	300	24	1·03	$1·0 \times 10^{-4}$
						Predicted $0·8 \times 10^{-4}$
		Reduction of titanic sulphate (II)				
25	2·5	100	976	1	0·36	$3·86 \times 10^{-3}$
4·7	4·66	10	461	1	0·68	$3·91 \times 10^{-3}$
0·47	4·66	1	458	1	0·67	$3·85 \times 10^{-3}$
0	4·66	0	451	1	0·66	$3·8 \times 10^{-3}$ †
						Predicted $3·8 \times 10^{-3}$

* Comparison of e with the hydrogen overpotential of mercury at the same c.d. in the supporting electrolyte showed that depolarisation was very large and therefore it could be assumed that $I' = I$. In these experiments, i was measured with a specially calibrated microammeter.

† Clearly, I' is limited by the rate of diffusion of depolariser to the cathode under the conditions used.

hydrogen ions and electrons to the depolariser seems more feasible than the direct addition of atomic hydrogen as usually postulated.

The prediction of the rate of chemical reduction from electroreduction data can only be made when the nature and the extent of the cathodic areas of the dissolving metal are known, *e.g.*, when the dissolving metal is pure and shows low anodic polarisation or when a metallic couple is being used. It is intended to present later an account of the reduction behaviour of metallic couples and also to extend the present comparison to group *B* reducing systems.

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